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Carborane-Catalyzed Graphitization in Polyarylacetylene-Derived Carbon–Carbon Composites

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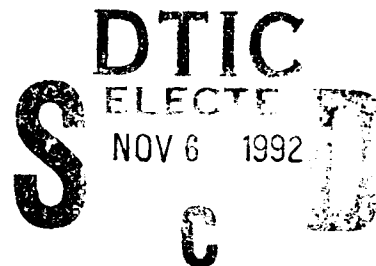P. O. Box 92960
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Boron in the form of a carborane compound, $C_2B_{10}H_{12}$, was used to catalytically graphitize a polyarylacetylene (PAA) resin, typically a nongraphitizing carbon, in bulk form and in a carbon–carbon (C/C) composite. In bulk form, significant graphitization was observed after heat treatment to 1800°C; complete graphitization was realized at 2400°C. Similar results were found for a PAA-derived carbon matrix in a unidirectional C/C composite.

The effect of carborane addition on the mechanical properties of C/C unidirectional composites of PAA and T-50 carbon fibers was also examined. After heat treatment to 1100°C, the tensile strength of unidirectional fiber tows increased significantly with increasing concentration of carborane. The increase in tensile strength was accompanied by increased fiber pullout, suggesting that interface weakening decreases the tendency for matrix-dominated brittle fracture. After heat treatment to 1800°C and above, the carborane decreased the strength of the composites but substantially increased the modulus.

Catalytic graphitization of PAA offers a major potential advantage of obtaining graphitic matrices in C/C without the disadvantages of conventional pitch processing. In addition, the much lower temperatures required for catalytic graphitization would enable processing temperatures for C/C to be reduced significantly.

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PREFACE

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FIGURES

I. INTRODUCTION

Carbon–carbon (C/C) composites are utilized for numerous severe-environment applications because of their light weight, high strength and modulus at elevated temperatures, and thermal stability. These properties make C/C composites ideal materials for aerospace applications, including rocket nozzles and exit cones.

The matrices in C/C composites vary from hard, glassy carbons to soft, graphitizing carbons. Hard or glassy carbons are typically derived from thermosetting resins. The most common, commercially available, thermosetting carbon precursor is phenolic resin (Fig. 1), a low-cost, easily fabricated carbon precursor. Phenolic resin has two principal disadvantages: low char yield, due to the presence of a large percentage of heteroatoms such as oxygen; and large shrinkage during carbonization. These two factors necessitate redensification. Pitch is a common, commercially available, soft, or graphitizing, carbon precursor. It undergoes a liquid crystalline (mesophase) transformation at – 400 to 500°C, enabling alignment of the large aromatic molecules that are the precursors to graphite (see Fig. 2). However, pitch is difficult to process and can have batch-to-batch inconsistencies because it is a derivative of coal and petroleum residues.

An alternative precursor for C/C composite matrices is polyarylacetylene (PAA). PAA is an experimental thermosetting resin synthesized from diethynylbenzene monomers. It was first synthesized in the late 1950s at the GE Research Laboratory as part of a search for high char yielding polymers. The early formulations underwent severe shrinkage and were highly exothermic during cure [2]. In the 1970s, Hercules patented a process [3] for the production of PAA by techniques that reduce the exotherm and shrinkage. Although the material was easier to process, composites made from the formulations were brittle and had poor structural integrity. In the early 1980s, The Aerospace Corporation's Materials Sciences Laboratory overcame these initial problems with PAA through the development of a low-temperature prepolymerization technique and polymer chain modifications [4,5].

The starting point for the polymerization is a cyclotrimerization reaction. Cyclotrimerization is a nickel-catalyzed prepolymerization in which three ethynyl groups react to form an aromatic ring (Fig. 3). The reaction is quenched to yield a low molecular weight "prepolymer." Use of the prepolymer substantially lowers the heat of reaction and therefore decreases the exotherm during composite processing; it also decreases the shrinkage during cure. The prepolymer is impregnated into fiber preforms and is thermally processed for cure, carbonization, and finally graphitization heat treatments. The residual nickel in the cured polymer is less than 0.1 wt.% and is not detectable by EDAX.

PAA is extremely attractive as a carbon precursor because of its very high carbon content, which results in a high char yield, as the thermogravimetric analysis plot of Fig. 4 demonstrates: The char yield for this PAA is approximately 88%, whereas that of the phenolic resin is only –50%. Low mass loss in PAA translates to low pyrolysis shrinkage, as indicated in

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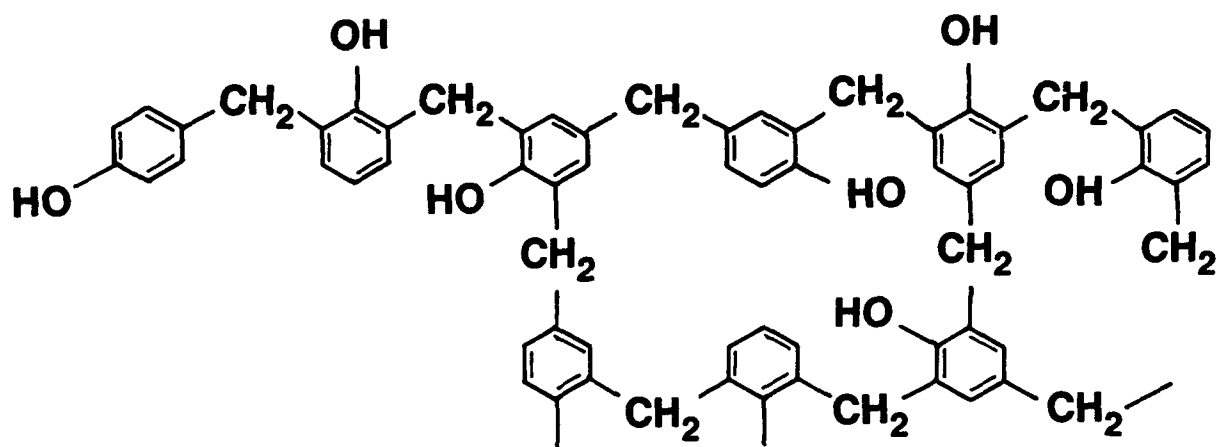
Figure 1. Chemical structure of typical phenol-formaldehyde resin.
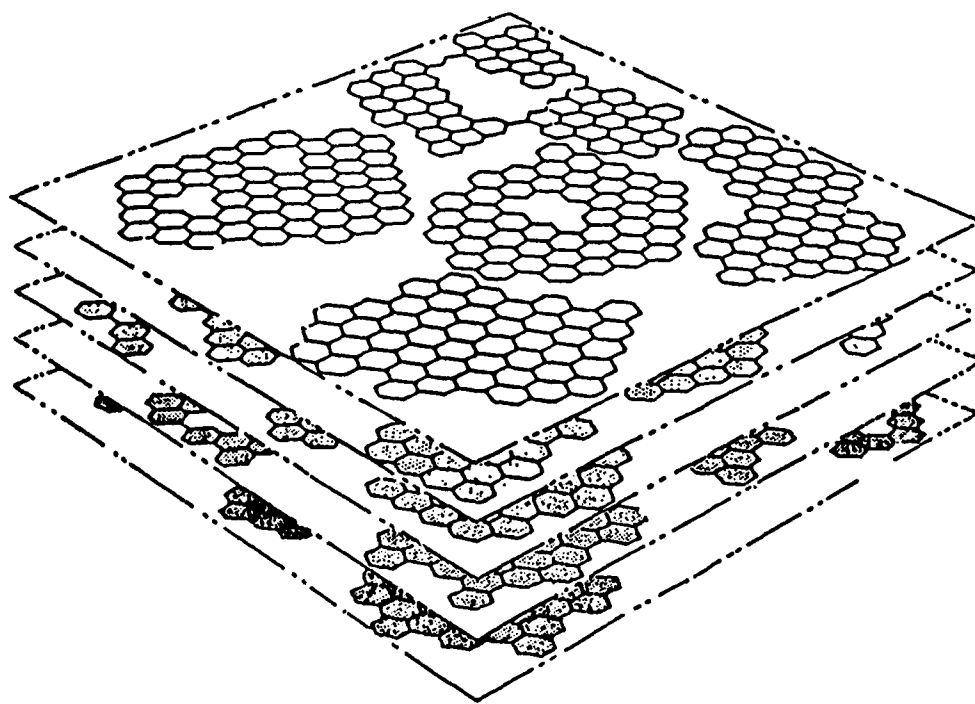
Figure 2. Schematic illustration of planar aromatic structure of liquid crystalline pitch mesophase according to Zimmer and White [1].

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CYCLOTRIMERIZATION
NICKEL CATALYST

DIETHYNYLBENZENE
MONOMER

POLYARYLACETYLENE (PAA)
"PREPOLYMER"

FIBERS
CURE
(heat, pressure)

PAA POLYMER
COMPOSITES

CARBONIZATION
(1000°C)

GRAPHITIZATION
(2400–2800°C)

CARBON-CARBON
COMPOSITES
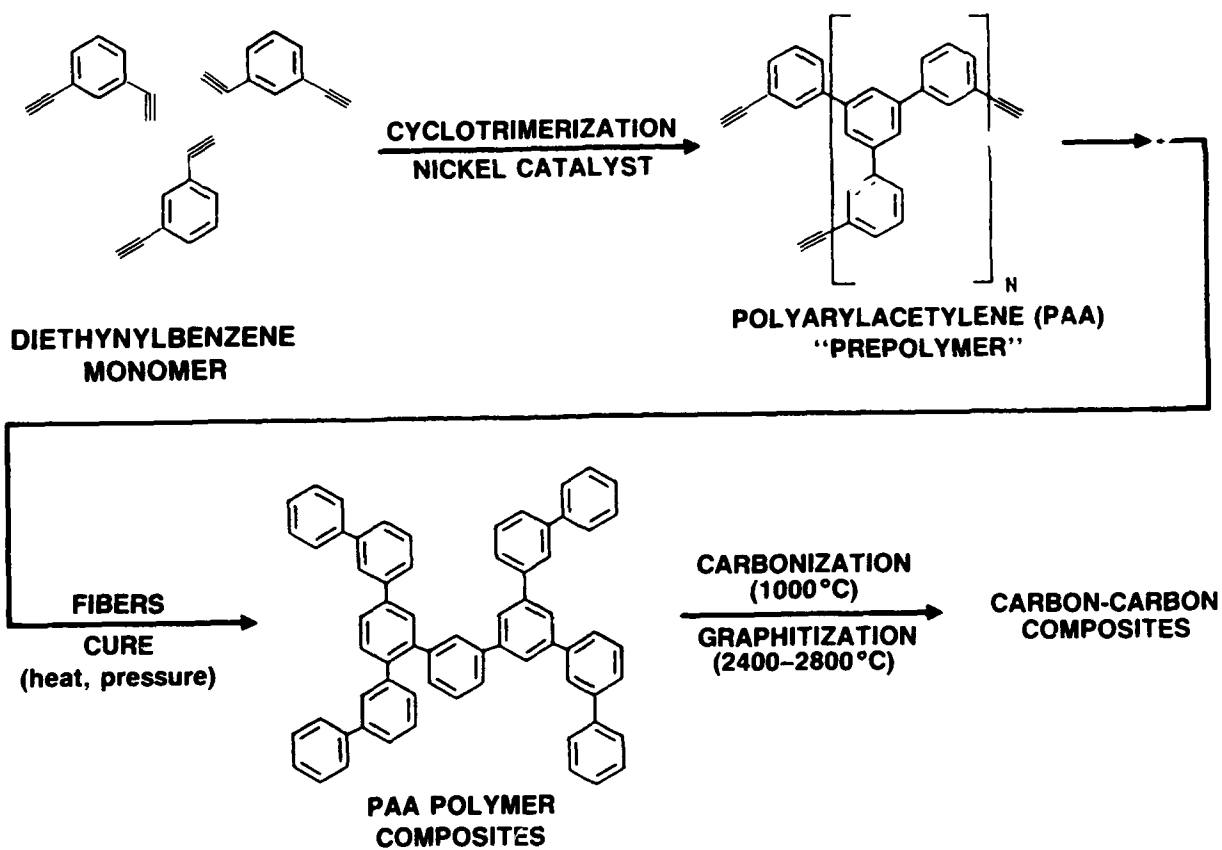
Figure 3. Chemical structure and processing of polyarylacetylene-based composites.
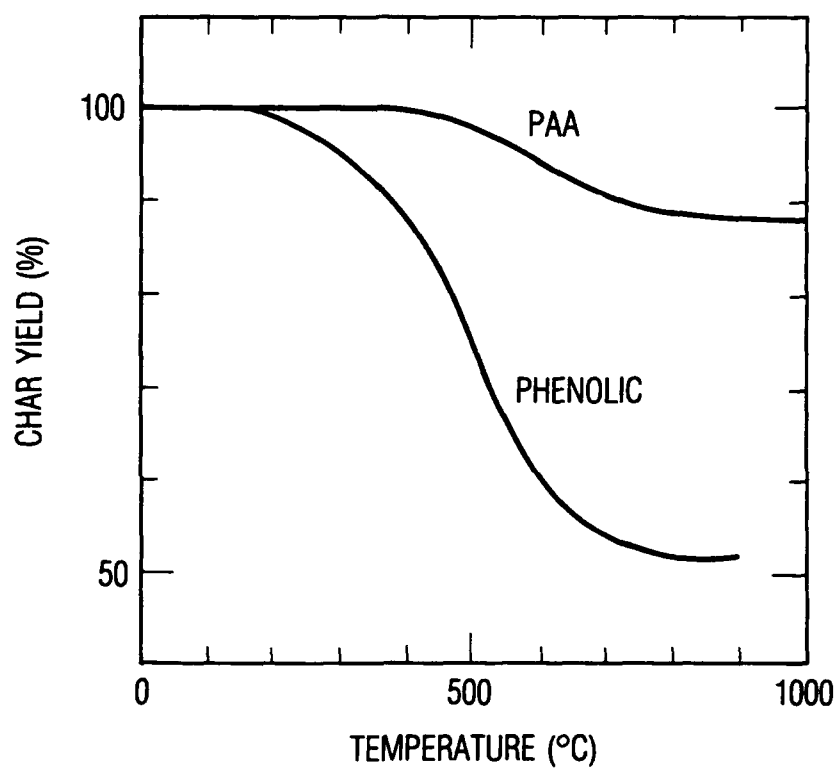
Figure 4. Thermogravimetric an lysis of PAA and phenolic resin.

Fig. 5 for PAA and a phenolic resin. At 750°C, PAA has only an 8% linear shrinkage compared with 20% for the phenolic resin.

Lower mass loss and shrinkage offer the potential for less fiber–matrix debonding. This is illustrated in Fig. 6, which compares the scanning electron micrographs of phenolic- and PAA-derived C/C composites heat-treated to 2400°C. Unlike PAA, the phenolic-derived composite shows an area in which the matrix has debonded from the fibers. One of the desirable goals in C/C technology is to combine the processing advantages of a thermosetting resin with the structural characteristics of a graphitizing matrix. For example, White and Sheaffer [6] have shown that mesophase pitches can be oxidized "in place" to prevent bloating during pyrolysis, while still maintaining the graphitizing character of the mesophase pitch. In addition to the enhanced toughness associated with a graphitic matrix, the increasing demand for lightweight radiator panels for space structures has focused attention on the thermal conduction properties of C/C. Using a standard aerospace PAN-based carbon fabric, ACC-4, it was shown recently [7] that across-ply thermal conductivity (from 400 to 1500°F) could be increased by over 200% using a pitch matrix instead of the standard phenolic-resin-based matrix.

Clearly, then, one limitation to the possible use of PAA as a carbon matrix precursor has been the inability to increase its crystallinity significantly. In order for the crosslinked polymer to rearrange and form a graphitic structure, carbon-to-carbon bonds must be broken and subsequently rearranged. Such an energy barrier is not easily overcome, even upon heat treatments in excess of 2800°C. As a result, bulk PAA, like other thermoset resins, forms poorly ordered glassy or vitreous carbons. Within a composite, however, PAA undergoes localized graphitization around the fiber (Fig. 6). Nevertheless, most of the matrix remains glassy. Therefore, in an effort to control the crystallization of PAA-derived carbon, we investigated the use of boron as a graphitization catalyst in the PAA.

Boron has been shown to be an effective graphitizing catalyst for various cokes and resins [8,9]. In high concentrations (of the order of 5 wt.%), boron can form B_4C, which can migrate through and convert carbon to a more ordered state. Boron can also decrease the kinetic barriers to graphitization by a vacancy diffusion mechanism at concentrations up to about 1 wt.% (the solubility limit is about 2 wt.%) [9,10].

Our approach in this study in using carborane was to determine the effect of this graphitization catalyst on the properties of both bulk PAA and C/C composites derived from PAA.

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Figure 5. Pyrolysis shrinkage of PAA and phenolic resin.

12

(a)

10 μm

(b)

7 μm

Figure 6. Nonuniform graphitization at 2400°C of glassy matrix C/C composites: (a) phenolic-derived composite and (b) PAA-derived composite.
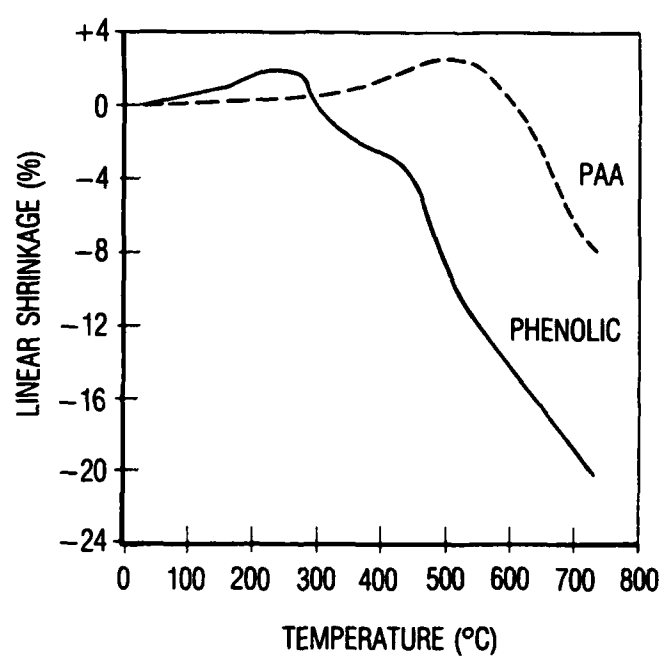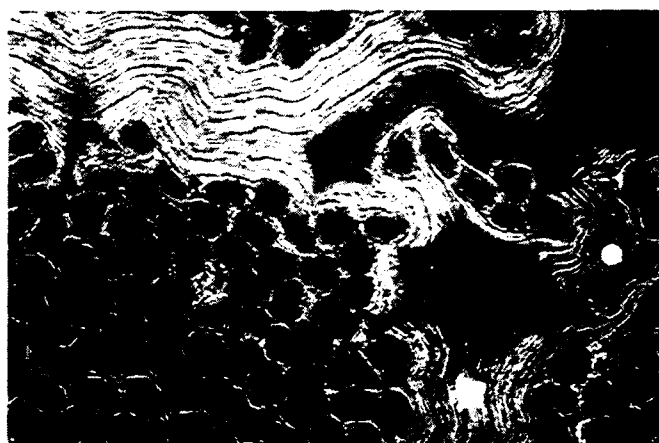
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II. EXPERIMENTAL

The catalyst used in this study was boron (B) introduced in the form of a carborane, $C_2B_{10}H_{12}$. The carborane was selected for its solubility in the PAA/methyl ethyl ketone (MEK) prepregging solution, which resulted in a homogeneous distribution of the carborane in the composite. A carborane/MEK mixture was prepared and then distilled to remove water as well as to disperse the carborane. The mixture was permitted to cool to room temperature under a nitrogen atmosphere, and the PAA prepolymer was slowly added to the stirring solution. Three solutions of carborane/PAA were made: 1, 3, and 5 wt.% boron. A small portion of each of the solutions was set aside for composite impregnation, and the remainder of the mixture was distilled on a roto-evaporation device to remove solvent. The resulting powder, as well as powder from undoped PAA, was cured at 250°C in a mold under ~ 400 psi. The neat PAA and doped PAA samples were then carbonized under flowing nitrogen to 1100°C. Some of the samples were further heat-treated under argon to 1800 or 2400°C for 1 hr.

The heat-treated, doped and undoped, bulk PAA samples were examined by X-ray diffraction performed by copper (Kα) radiation, using a computer-controlled vertical powder diffractometer equipped with a graphite crystal monochromator and a scintillation detector. The graphite (002) reflection was scanned from 22° to 29° at a speed of 2.4°/min and operating conditions of 45 kV and 38 mA.

Fiber-reinforced unidirectional samples were prepared using Amoco PAN-based T–50 carbon fibers with 3000 filaments/bundle. The T–50 fibers were wound on a rack and impregnated with either the carborane-doped or the undoped PAA solution. The impregnated tows were permitted to air-dry, thereby evaporating the residual MEK. The tows were then cut to 6-in. lengths. Two hundred impregnated tows were placed into a 6 × 0.5 in. mold and cured to 250°C under 300 psi pressure (Fig. 7). The unidirectional composites were heat-treated to 1100°C under nitrogen to carbonize the matrix, and some samples were subsequently heat-treated to 1800 or 2400°C under argon. All samples were held for 1 hr at the heat-treatment temperature (HTT).

In addition to the unidirectional composites, individual tows were impregnated, cured, and heat-treated to 1100, 1800, or 2400°C under an inert atmosphere. Those tows were used for mechanical testing of the carborane-doped PAA. The strength and modulus were measured using an Instron tensile tester with a crosshead speed of 0.02 in./min. The gage length of all the samples was 2 in.

The fiber-reinforced samples were examined by a scanning electron microscope (SEM). With the exception of the fracture specimens, the unidirectional composites were mounted in epoxy and polished to a 1 μm finish. The samples were then xenon-ion-etched. This technique has been shown [11] to enhance the distinction between glassy and graphitic-type carbon microstructures, owing to differential etching rates in anisotropic graphite crystallites.

Ion microprobe mass analysis (IMMA) was used to identify the location of the boron within the B-doped composites. The 1% carborane samples were examined after heat treatments to 1200 and 2400°C. In addition, the 3 and 5% carborane samples heat-treated to 2400°C were examined.
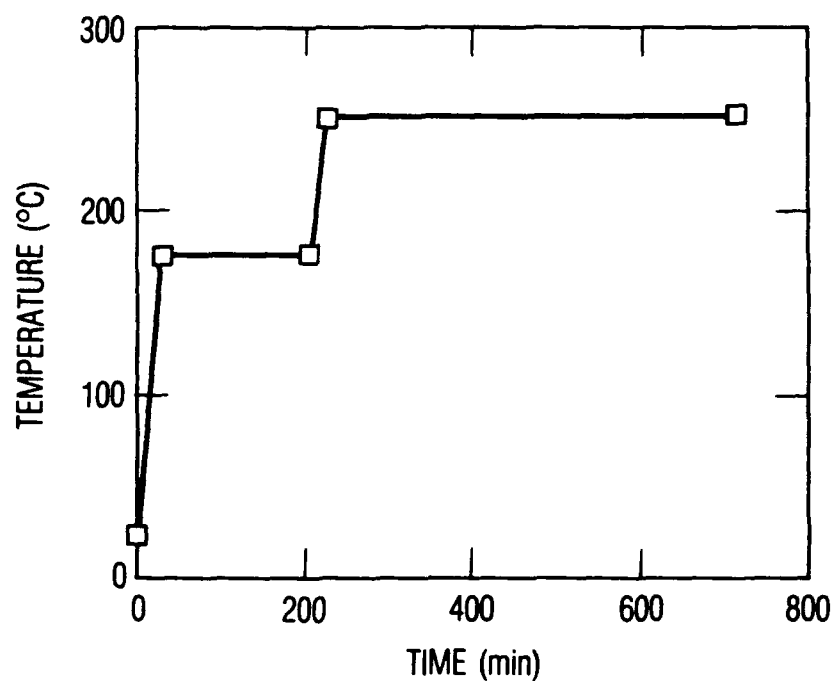

Figure 7. PAA cure schedule.

III. RESULTS

X-ray diffraction profiles of the 5% carborane-doped and undoped PAA samples heat-treated to various temperatures are shown in Figs. 8 through 10. The profiles of the doped and undoped PAA heat-treated to 1100°C are essentially the same (Fig. 8). Upon further heat treatment to 1800°C (Fig. 9), the undoped PAA is unchanged (note different scales). In contrast, there is a dramatic increase in the crystallinity of the 5% B-doped PAA; the position of the diffraction peak corresponds to an interlayer spacing d(002) of − 3.38 Å. At 2400°C (Fig. 10), the undoped PAA remains amorphous while the d(002) of the doped material has decreased further to 3.364 Å. At 2800°C, the d(002) decreases to 3.359 Å, closely approaching that of graphite, 3.354 Å.

The effect of the carborane dopant on the matrix microstructure within the unidirectional PAA composites after further heat treatment is shown in Figs. 11 and 12. After heat treatment to 1800°C (Fig. 11), the ion-etched matrix within the undoped PAA has no texture, i.e., no lamellar features, indicating a glassy structure. The matrix in the 5% carborane-doped PAA appears to have some slight texture, indicating the beginning development of crystalline structure. Upon further heat treatment to 2400°C (Fig. 12), a small amount of localized graphitization is evident in the undoped PAA composite, but large areas of matrix are still glassy. Once again, the most dramatic change is found within the 5% sample where the matrix is completely graphitized. At the higher magnification, that matrix reveals distinct graphitic lamellae.

The results of room-temperature tensile testing of single-tow composites are shown in Figs. 13 and 14. Figure 13 is a plot of tensile strength versus HTT for the undoped and 1%, 3%, and 5% carborane-doped PAA tows. Each plotted data point represents the average of 20 values. The line connects the tensile strength of undoped PAA for the various heat treatments. Because of the large difference in fiber and matrix moduli, strength and modulus values are calculated relative to the fiber cross-sectional areas to yield an effective, *in situ* fiber strength and modulus. For the undoped composite with a heat treatment to 250°C (the cured state), average filament strength is 2.4 GPa (350 kpsi), which agrees well with the tensile strengths reported by Amoco. Upon further heat treatment to 1100°C, a sharp drop occurs in the composite tensile strength. This drop is due to the conversion of the matrix from a relatively compliant polymer to a low-strain-to-failure carbon. Since the matrix remains well bonded and is brittle after heat treatment to 1100°C, a flaw or crack initiated in the matrix can propagate through the fibers, resulting in a catastrophic failure. The composite therefore behaves more like a monolithic solid following a Griffith-type failure.

An increase in tensile strength is observed upon further heat treatments to 1800 and 2400°C, and is postulated to be due to one or a combination of several mechanisms. One possible mechanism is associated with the conversion of the matrix from amorphous carbon to a higher-strain-to-failure graphitic-type structure. Another possible mechanism is the weakening of the fiber–matrix interface owing to the more graphitic matrix structure; it results in the

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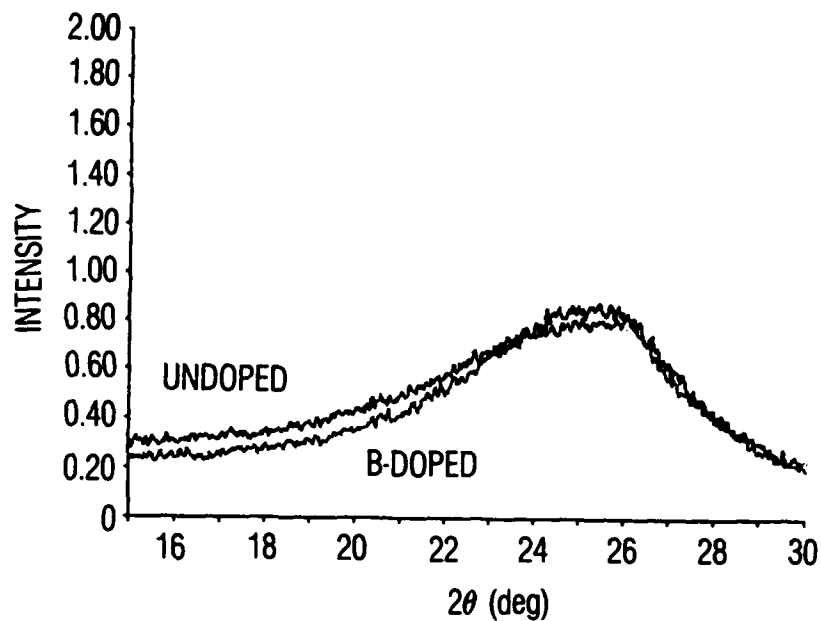
Figure 8. X-ray diffraction of undoped and 5% B-doped PAA-derived carbon heat-treated to 1200°C.
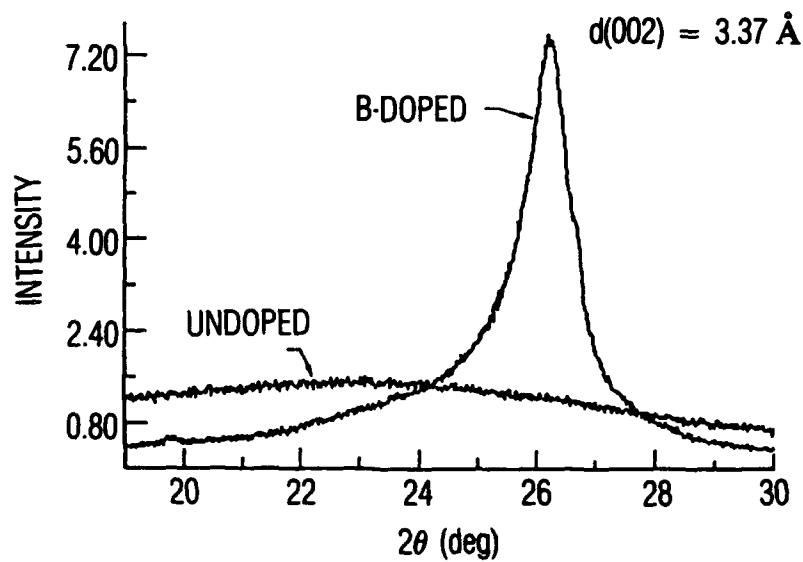
Figure 9. X-ray diffraction of undoped and 5% B-doped PAA-derived carbon heat-treated to 1800°C.

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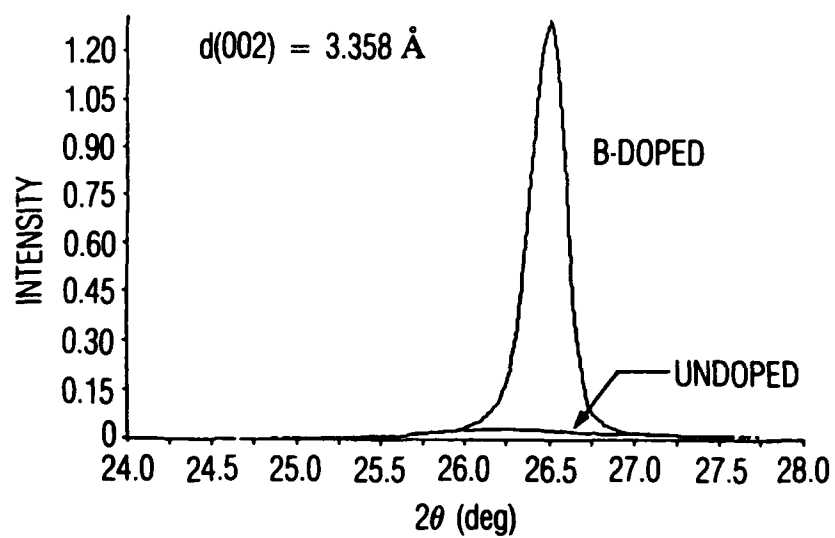
Figure 10. X-ray diffraction of undoped and 5% B-doped PAA-derived
carbon heat-treated to 2400°C.

Figure 11. Cross-sectional view of PAA-derived C/C composites heat-treated to 1800°C: (a) undoped and (b) 5% B-doped.

Figure 12. Cross-sectional view of PAA-derived C/C composites heat-treated to 2400°C: (a) undoped and (b) 5% B-doped.

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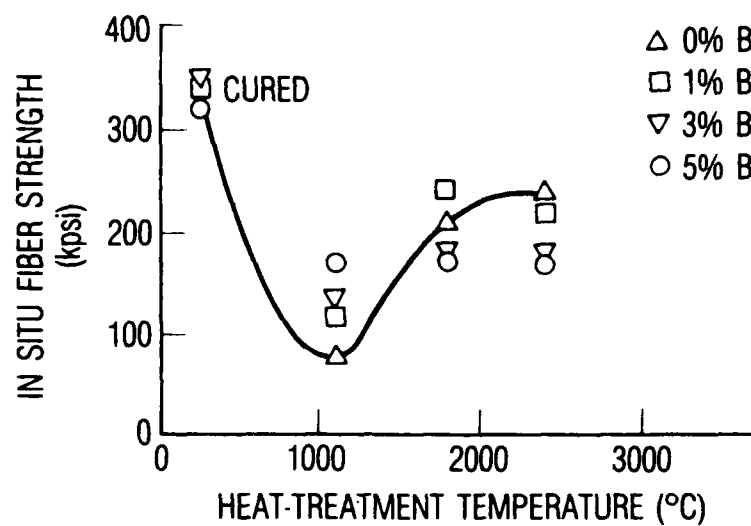
Figure 13. Tensile strength of B-doped PAA/T-50 C/C tows (uncertainty is approx. ± 5-10%).
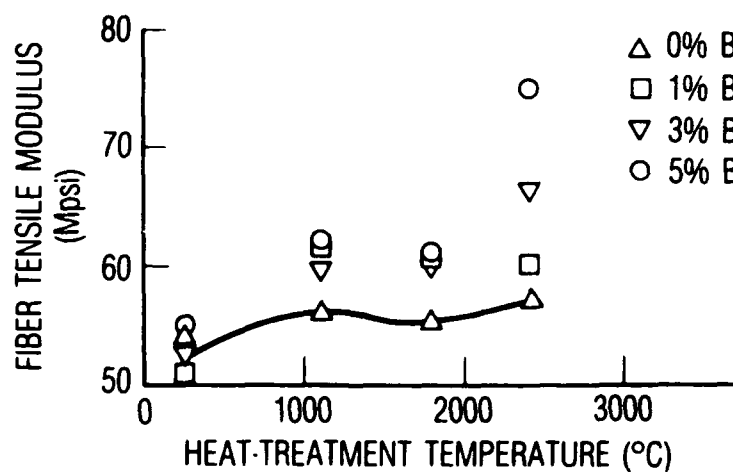
Figure 14. Elastic modulus of B-doped PAA/T-50 C/C tows (uncertainty is approx. ± 5-10%).

fracture of the composite being less matrix dominated and, therefore, permits higher strain to failure of the fiber. Weak interfaces in composites with brittle matrices are known to act as crack deflectors [12], thereby increasing composite toughness.

At 1100°C, there is an increase in tensile strength with an increase in boron concentration. Figures 15a and 15b show SEM fracture surfaces of both an undoped and a 5% carborane-doped composite heat-treated to 1100°C, respectively. The undoped composite behaves as a monolithic solid and fractures in a planar-catastrophic mode. Increasing boron concentration results in increasing fiber pullout, which is a typical toughening mechanism and indicates a weakened interface. The 5% B-doped sample (Fig. 15b) exhibits the largest degree of fiber pullout. However, since the SEMs and X-ray diffraction at 1100°C show no indication of matrix graphitization, the reason for the weakened interface is unclear.

Further heat treatment of carborane-doped composites to 1800°C reveals an increase in strength for the 1% B-doped system and a decrease at the higher concentrations. Figure 16a shows the fracture surface of an undoped C/C composite heat-treated to 1800°C; the fracture surfaces of the 3 and 5% doped samples had the same brittle-type appearance. The fracture surface of the 1% sample is shown in Fig. 16b and reveals a large degree of fiber pullout.

At 2400°C, all B-doped composites show a decrease in strength relative to the undoped composites. For this HTT, there is also a sharp increase in the Young's modulus with increasing boron concentration. Such a large increase can only be explained by an increase in the modulus of the fiber, most probably caused by solid-state diffusion of the boron from the matrix into the carbon fibers, resulting in increased fiber graphitization. Ezekiel [13] reported that boron additions of 0.1 to 1.0% increase the rate of graphitization of carbon fibers. He obtained modulus increases of up to 300%.

IMMA results (Figs. 17 through 20) were performed to study the distribution of boron in the composites. Figure 17a is the IMMA boron mapping of a 1% carborane-doped PAA composite heat-treated to 1800°C, and Fig. 17b is the optical micrograph of the same area. As shown, the boron is evenly dispersed throughout the matrix but cannot be identified within the fiber. Nevertheless, the lower failure strengths of the 3 and 5% boron samples after the 1800°C HTT suggest some alteration of the fiber or fiber–matrix interface properties which is not detectable by IMMA.

As the HTT is increased to 2400°C, boron migrates into the fiber, as shown in Fig. 18, and appears to be more or less evenly dispersed. The higher concentration B-doped composites (3 and 5%) after the 1-hr heat treatment at 2400°C (Figs. 19 and 20) also display migration of boron into the fibers, but the distribution is less uniform.

Figures 21a and 21b show the fracture surfaces of both an undoped and a B-doped composite heat-treated to 2400°C. The undoped sample appears to show some pullout. In contrast, the B-doped C/C composite, surprisingly, now displays much less pullout than fracture surfaces of

(a)

(b)

Figure 15. SEM fracture surface of (a) undoped and (b) B-doped PAA-
derived C/C tows heat-treated to 1100°C.

(a) (b)

Figure 16. Fracture surface of (a) undoped and (b) B-doped PAA-
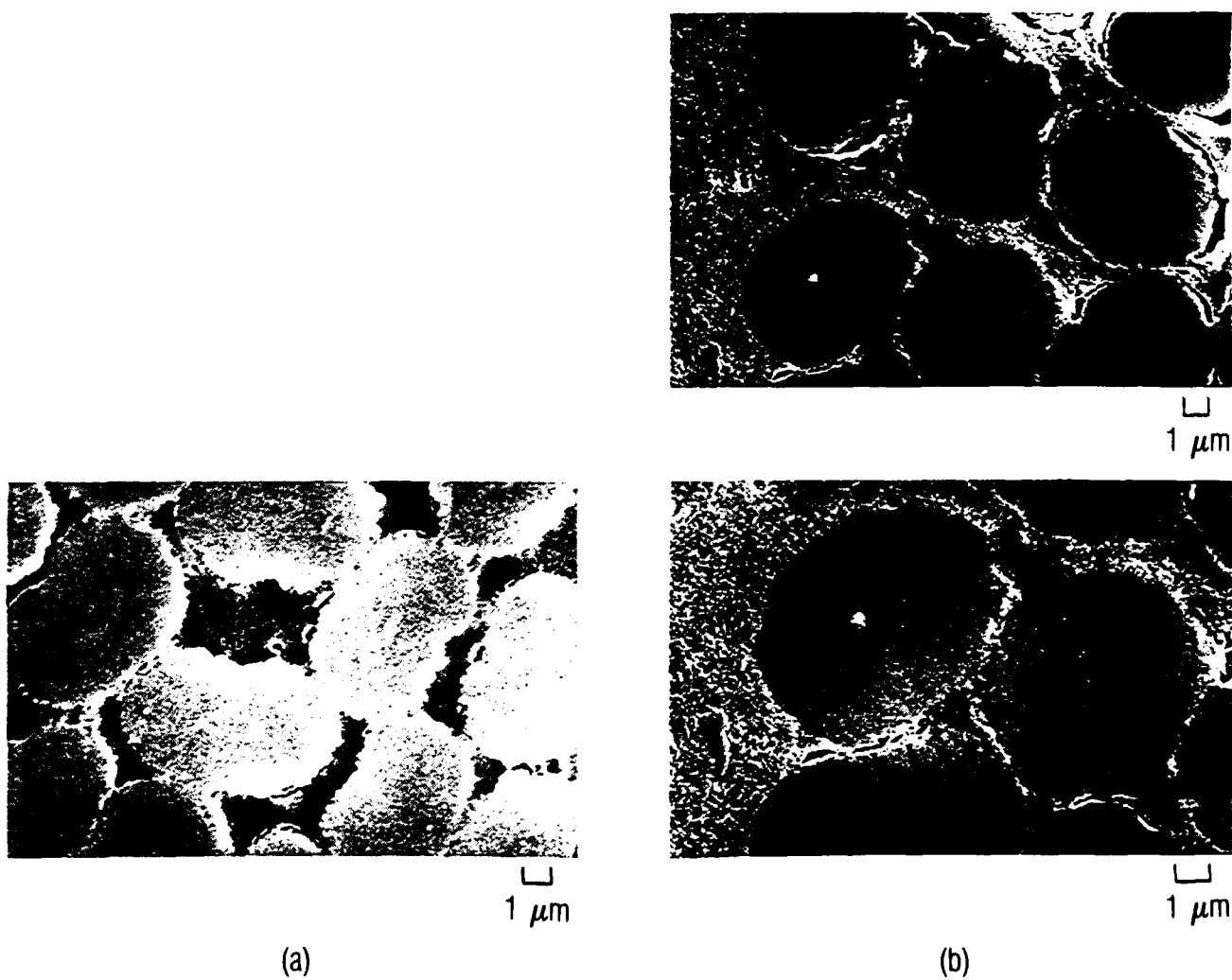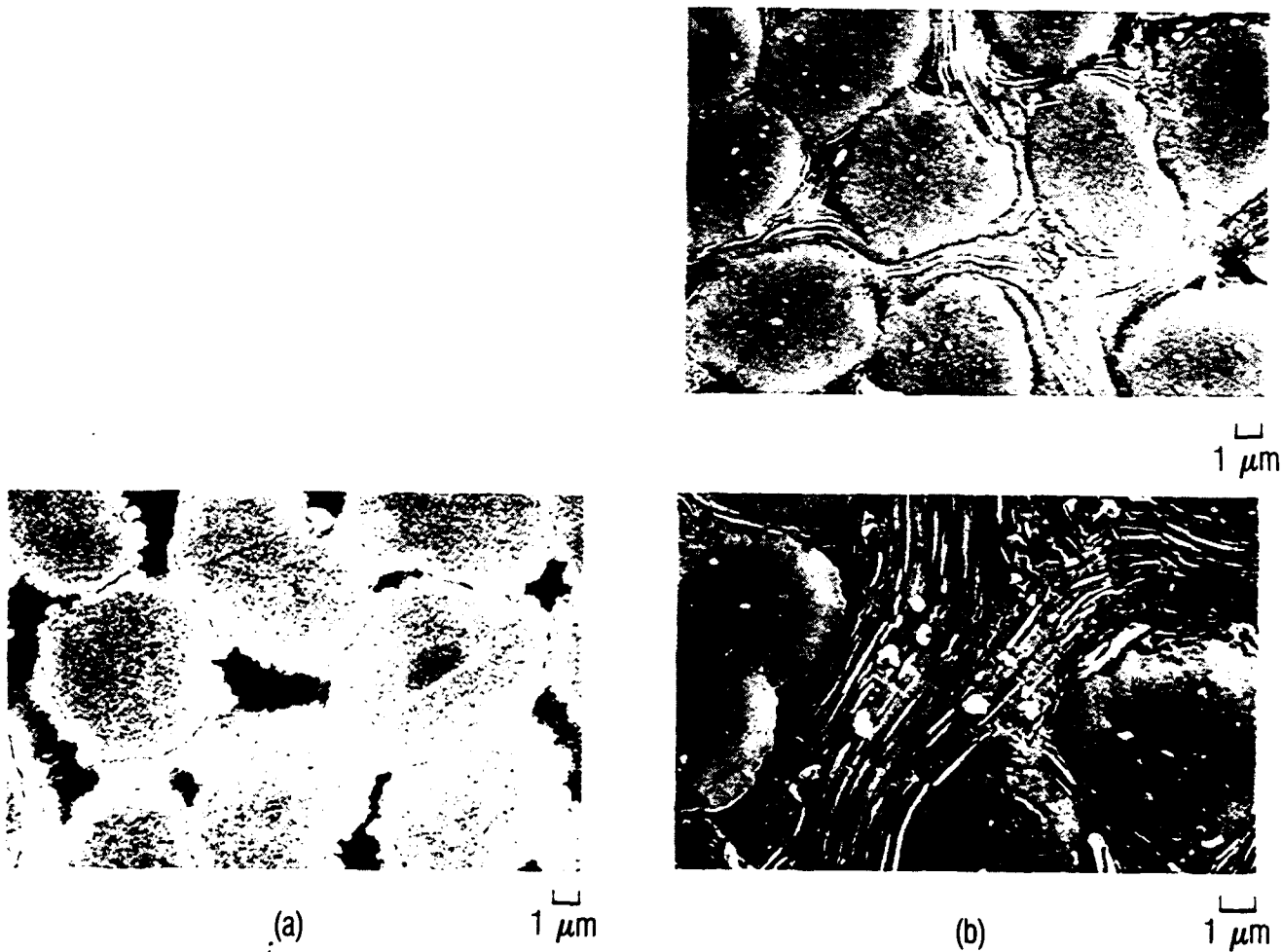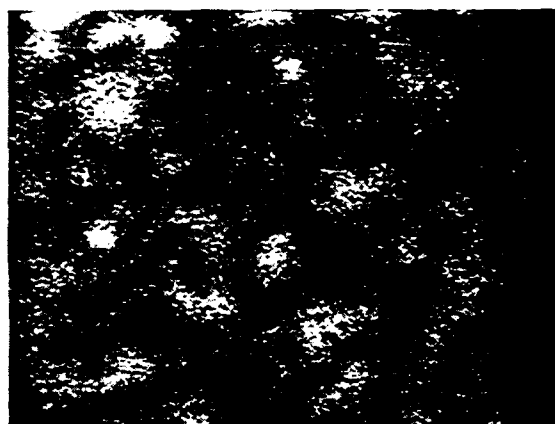derived C/C tows heat-treated to 1800°C.

(a)

10 μm

(b)
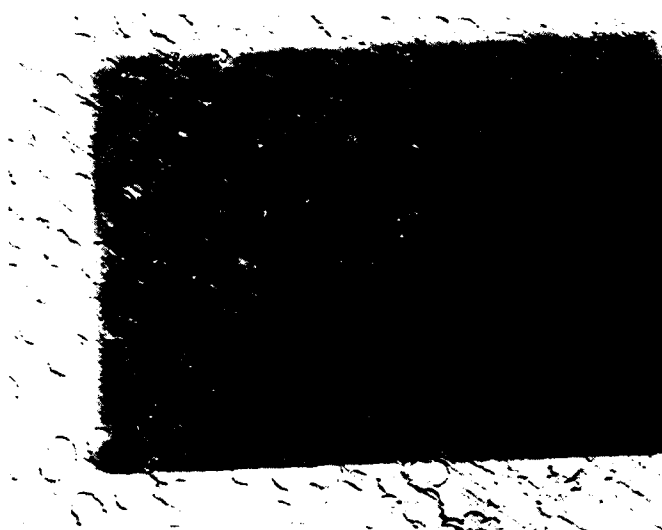
10 μm

Figure 17. (a) IMMA scan of a 1% B-doped PAA-derived C/C composite after heat treatment to 1800°C, showing distribution of boron in matrix. (b) Photomicrograph of the same area in (a).

Figure 18. IMMA scan of a 1% B-doped PAA-derived C/C composite after heat treatment to 2400°C.

Figure 19. IMMA scan of a 3% B-doped PAA-derived C/C composite after heat treatment to 2400°C.

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10 μm
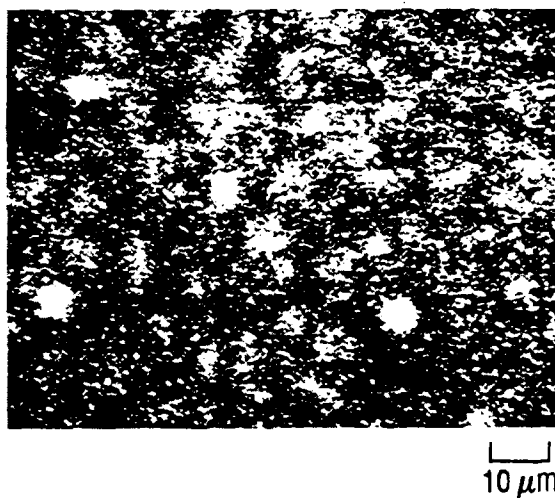
Figure 20. IMMA scan of a 5% B-doped PAA-derived C/C composite
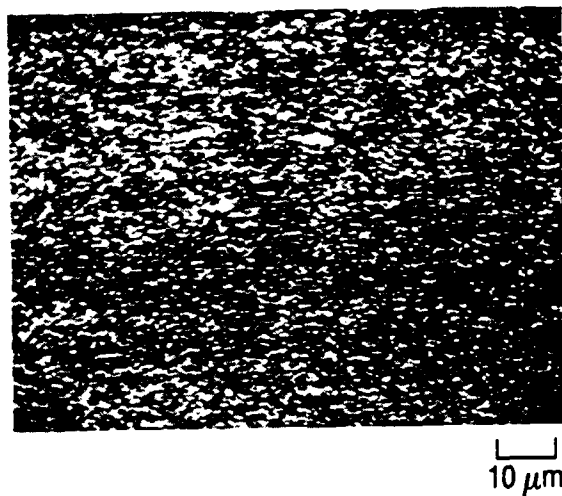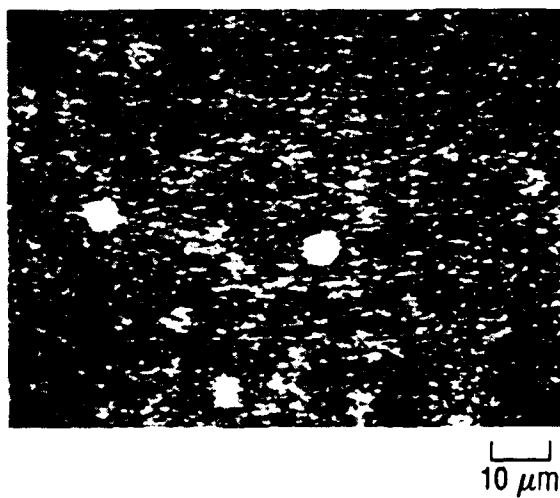after heat treatment to 2400°C.

the lower temperature samples, suggesting an increase in the fiber–matrix interface strength. However, if the fiber is more graphitic at 2400°C, as the modulus and IMMA results suggest, we would expect weakening of the fiber–matrix interface and increased fiber pullout. Clearly, more work is needed to define the mechanisms by which boron affects the matrix and fibers and, hence, the mechanical properties of C/C composites.

100 μm

(a)

100 μm

(b)

Figure 21. Fracture surface of (a) undoped and (b) B-doped PAA-derived C/C tows heat-treated to 2400°C.

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IV. CONCLUSIONS

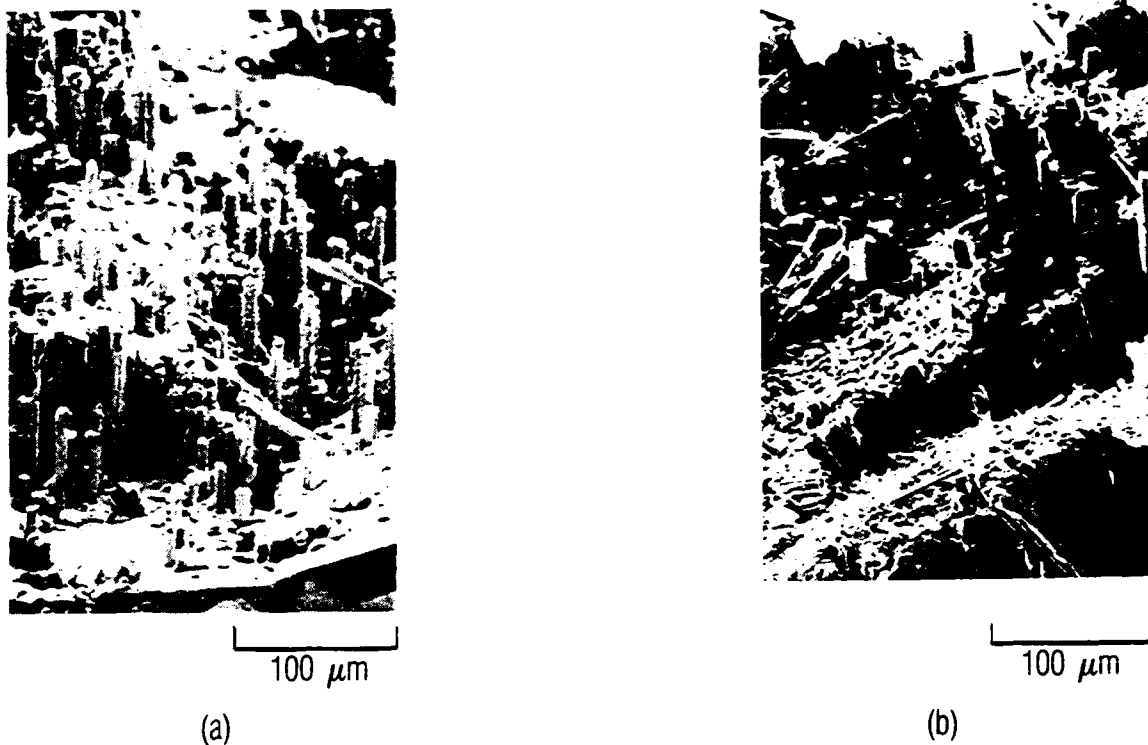The effect of carborane addition on the microstructure of PAA was examined. PAA, a glassy carbon precursor, is catalytically transformed to a graphitic-type carbon in the bulk form and as a C/C matrix material. The extent of graphitization is controlled by the amount of catalyst present and the heat-treatment temperatures. The onset of catalytic graphitization occurs at temperatures much lower than typically used in C/C processing; therefore, it may be possible to reduce HTTs for C/C composites. The controllability of the catalytic graphitization enables a homogeneous matrix to form. A major advantage to this approach lies in the easy process-ability of PAA relative to coal-tar and petroleum pitches.

The addition of boron affects the mechanical properties in several ways. The modulus of PAA-derived C/C composites increases with HTTs of 1800°C and higher. For an 1100°C heat treatment, the tensile strength increases with increasing concentration of boron dopant. The strength at 1800°C can increase or decrease depending on boron level. Lastly, with a 2400°C heat treatment, the strength falls off at all boron levels, due apparently to catalytic graphitiza-tion of the fibers.

Further work is needed to clarify the mechanisms by which boron alters the properties of C/C composites. Of principal interest are 1) identifying the distribution, and chemical and physi-cal form, of boron within the fiber and matrix constituents (i.e., substitutional or interstitial), and 2) separating the effects of boron catalysis from simple boron addition.

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